Multiply subtractive Kramers-Krönig relations for arbitrary-order harmonic generation susceptibilities

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Kramers-Krönig (K-K) analysis of harmonic generation optical data is usually greatly limited by the technical inability to measure data over a wide spectral range. Data inversion for real and imaginary part of $\chi^n(n\omega;\omega,...,\omega)$ can be more efficiently performed if the knowledge of one of the two parts of the susceptibility in a finite spectral range is supplemented with a single measurement of the other part for a given frequency. Then it is possible to perform data inversion using only measured data and subtractive K-K relations. In this paper multiply subtractive K-K relations are, for the first time, presented for the nonlinear harmonic generation susceptibilities. The applicability of the singly subtractive K-K relations are shown using data for third-order harmonic generation susceptibility of polysilane.

1 Introduction

In linear optics Kramers-Krönig (K-K) relations and sum rules for linear susceptibility, $\chi^{(1)}(\omega)$, constitute well-established tools of fundamental importance in the analysis of linear optical data, since they relate refractive and absorptive phenomena and provide the possibility to check the self-consistency of experimental or model-generated data [1–4]. The foundation of these fundamental integral relations lies in the principle of causality in the response of the matter to the external radiation, the conceptual bridge being established by the Titchmarsh's theorem [5].

Much effort has been placed in a very wide and detailed theoretical and experimental investigation of nonlinear optical processes due to their huge scientific

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and technological relevance. Apart from results relative to specific cases [6–8], a more modern approach to the problem of framing in a coherent and general fashion dispersion theory of the nonlinear susceptibilities has started recently dating back to the late 1980s [9,10] and early 1990s [11–13].

In the case of harmonic wave generation, which is probably the single most representative process of all the nonlinear optical phenomena, only recently a complete formulation of general K-K relations and sum rules for nth order harmonic generation susceptibility $\chi^{(n)}(n\omega;\omega,\cdots,\omega)$ has been obtained [14–16]. Unfortunately, even now there are relatively few studies that report on independent measurements of the real and imaginary parts of the harmonic generation susceptibilities [17,18], and on the validity of K-K relations in nonlinear experimental data inversion [19].

Characteristic integral structure of K-K relations requires the knowledge of the spectrum at a semi-infinite angular frequency range. Unfortunately, in practical spectroscopy only finite spectral range can be measured. The technical problem to measure nonlinear optical spectrum at relatively wide energy range is probably the single most important reason why experimental research in this field has been depressed for a long time. Fortunately, recent development of dye lasers is very promising. However, at the moment such lasers seem to have relevance in nonlinear optical spectroscopy for relatively low order nonlinear processes.

In the context of linear optics singly [20] (SSKK) and multiply [21] subtractive Kramers-Krönig (MSKK) relations have been proposed in order to relax the limitations due to finite-range data. As far as we know, they have never been proposed for nonlinear susceptibilities and especially for harmonic generation susceptibilities. The idea behind the subtractive Kramers-Krönig technique is that the inversion of the real (imaginary) part of $\chi^{(n)}(n\omega;\omega,\cdots,\omega)$ can be greatly improved if we have one or more anchor points, i.e. a single or multiple measurement of the imaginary (real) part for a set of frequencies. In such a case we give general expressions for multiply subtractive K-K relations having a faster convergence, thus decreasing the error due to the inevitable finite spectral range.

This paper is organized as follows. In Section 2 we give the expressions for multiply subtractive K-K relations for $\chi^{(n)}(n\omega;\omega,\cdots,\omega)$ and in Section 3 we present application of SSKK on experimental data of third-order harmonic generation susceptibility of polysilane. Finally, in Section 4 we set our conclusions.

2 Multiply subtractive K-K relations for $\chi^{(n)}(n\omega;\omega,...,\omega)$

The analysis of the holomorphic [2] properties of the nth order harmonic generation susceptibility, which intrinsically derive from the principle of causality in the nonlinear response function of the matter [22], allows the derivation of the following Hilbert transform [11]:

$$\imath\pi\chi^{(n)}(n\omega';\omega',\cdots,\omega') = \wp\int_{-\infty}^{\infty}\frac{\chi^{(n)}(n\omega;\omega,\cdots,\omega)}{\omega'-\omega}\mathrm{d}\omega, \tag{1}$$

where $\wp$ indicates the Cauchy principal part integration. With the aid of the symmetry relation

$$\chi^{(n)}(n\omega;\omega,\cdots,\omega) = [\chi^{(n)}(-n\omega;-\omega,\cdots,-\omega)]^* \tag{2}$$

with (*) denoting the complex conjugation, we obtain the following K-K relations for the real and imaginary parts:

$$\Re\{\chi^{(n)}(n\omega')\} = \frac{2}{\pi}\wp\int_0^{\infty}\frac{\omega\Im\{\chi^{(n)}(n\omega)\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \tag{3}$$

$$\Im\{\chi^{(n)}(n\omega')\} = -\frac{2\omega'}{\pi}\wp\int_0^{\infty}\frac{\Re\{\chi^{(n)}(n\omega)\}}{\omega^2-\omega'^2}\mathrm{d}d\omega, \tag{4}$$

where, for the sake of clarity, we denote $\chi^{(n)}(n\omega;\omega,\cdots,\omega)$ simply by $\chi^{(n)}(n\omega)$. The independent dispersion relation (3) in principle allows us to compute the real part of the susceptibility once we know the imaginary part for all frequencies and *vice versa*.

Palmer *et al*. [21] have studied multiply subtractive K-K analysis in the case of phase retrieval problems related to linear reflection spectroscopy. Here their results are generalized to hold for holomorphic nonlinear susceptibilities. Unfortunately, Palmer *et al*. [21] presented MSKK only for the phase angle (imaginary part of the linear reflectance). Here we extend their theory to hold both for the real and imaginary parts of the arbitrary-order harmonic generation susceptibility. With the aid of mathematical induction (see appendix A in ref. [21]) we can derive the multiply subtractive K-K relation for the real and imaginary parts as follows:

$$
\begin{aligned}
&\Re\{\chi^{(n)}(n\omega')\} \\
&\quad= \left[\frac{(\omega'^2-\omega_2^2)(\omega'^2-\omega_3^2)\cdots(\omega'^2-\omega_Q^2)}{(\omega_1^2-\omega_2^2)(\omega_1^2-\omega_3^2)\cdots(\omega_1-\omega_Q^2)}\right]\Re\{\chi^{(n)}(n\omega_1)\}+\cdots \\
&\quad+\left[\frac{(\omega'^2-\omega_1^2)\cdots(\omega'^2-\omega_{j-1}^2)(\omega'^2-\omega_{j+1}^2)\cdots(\omega'^2-\omega_Q^2)}{(\omega_j^2-\omega_1^2)\cdots(\omega_j^2-\omega_{j-1}^2)(\omega_j^2-\omega_{j+1}^2)\cdots(\omega_j-\omega_Q^2)}\right]\Re\{\chi^{(n)}(n\omega_j)\}+\cdots \\
&\quad+\left[\frac{(\omega'^2-\omega_1^2)(\omega'^2-\omega_2^2)\cdots(\omega'^2-\omega_{Q-1}^2)}{(\omega_Q^2-\omega_1^2)(\omega_Q^2-\omega_2^2)\cdots(\omega_Q-\omega_{Q-1}^2)}\right]\Re\{\chi^{(n)}(n\omega_Q)\} \\
&\quad+\frac{2}{\pi}\left[(\omega'^2-\omega_1^2)(\omega'^2-\omega_2^2)\cdots(\omega'^2-\omega_Q^2)\right]\wp\int_0^\infty\frac{\omega\Im\{\chi^{(n)}(n\omega)\}\,\mathrm{d}\omega}{(\omega^2-\omega'^2)\cdots(\omega^2-\omega_Q^2)},
\end{aligned}
\tag{5}
$$

$$
\begin{aligned}
\frac{\Im\{\chi^{(n)}(n\omega')\}}{\omega'} &= \left[\frac{(\omega'^2-\omega_2^2)(\omega'^2-\omega_3^2)\cdots(\omega'^2-\omega_Q^2)}{(\omega_1^2-\omega_2^2)(\omega_1^2-\omega_3^2)\cdots(\omega_1-\omega_Q^2)}\right]\frac{\Im\{\chi^{(n)}(n\omega_1)\}}{\omega_1}+\cdots \\
&+\left[\frac{(\omega'^2-\omega_1^2)\cdots(\omega'^2-\omega_{j-1}^2)(\omega'^2-\omega_{j+1}^2)\cdots(\omega'^2-\omega_Q^2)}{(\omega_j^2-\omega_1^2)\cdots(\omega_j^2-\omega_{j-1}^2)(\omega_j^2-\omega_{j+1}^2)\cdots(\omega_j-\omega_Q^2)}\right]\frac{\Im\{\chi^{(n)}(n\omega_j)\}}{\omega_j}+\cdots \\
&+\left[\frac{(\omega'^2-\omega_1^2)(\omega'^2-\omega_2^2)\cdots(\omega'^2-\omega_{Q-1}^2)}{(\omega_Q^2-\omega_1^2)(\omega_Q^2-\omega_2^2)\cdots(\omega_Q-\omega_{Q-1}^2)}\right]\frac{\Im\{\chi^{(n)}(n\omega_Q)\}}{\omega_Q} \\
&-\frac{2}{\pi}\left[(\omega'^2-\omega_1^2)(\omega'^2-\omega_2^2)\cdots(\omega'^2-\omega_Q^2)\right]\wp\int_0^\infty\frac{\Re\{\chi^{(n)}(n\omega)\}\,\mathrm{d}\omega}{(\omega^2-\omega'^2)\cdots(\omega^2-\omega_Q^2)}.
\end{aligned}
\tag{6}
$$

Here ω_j with $j=1,\cdots,Q$ denote the anchor points. Note that the anchor points in Eqs. (5) and (6) need not to be the same. We observe that the integrands of Eqs. (5) and (6) have remarkably faster asymptotic decrease, as a function of angular frequency, than the conventional K-K relations given by Eqs. (3) and (4). This can be observed by comparing the integrands of K-K and MSKK relations since the convergence of Q-times subtracted K-K relations is proportional to $\omega^{-(2n+2+2Q)}$ whereas the conventional K-K relations decrease proportional to $\omega^{-(2n+2)}$. Therefore, it is expected that the limitations related to the presence of an experimentally unavoidable finite frequency range are thus relaxed, and the precision of the integral inversions is then enhanced.

Before proceeding we wish to remark that MSKK relations can also be written for all the moments $\omega'^{2\alpha}[\chi^{(n)}(n\omega';\omega',...,\omega')]^k$ with $0\le\alpha\le k(n+1)$, where α and k are integers. Such functions play an important role in the context of sum rules for arbitrary-order harmonic generation susceptibilities [14–16].

Palmer *et al*. [21] discussed how the anchor points should be chosen inside the measured spectral range. It is well known that Chebyshev polynomials have great importance in minimizing errors in numerical computations [23].

According to Palmer *et al.* [21] accurate data inversion is possible when the anchor points are chosen near to the zeros of the Qth order Chebyshev polynomial of the first kind. In linear optical spectroscopy it is usually easy to get information of the optical constants at various anchor points. However, in the field of nonlinear optics it is difficult to obtain the real and imaginary parts of the nonlinear susceptibility at various anchor points. Therefore, in the present study we wish to emphasize that even a single anchor point reduces the errors caused by finite spectral range in data inversion of nonlinear optical data. Then the choice of the location of the anchor point is not critical as concerns the coincidence of the zero of the Chebyshev polynomial. Furthermore, the Chebyshev zeros accumulate at the ends of the data interval. This is the reason why the anchor point is chosen near to one end of the data interval. For one anchor point, say at frequency ω_1, we obtain from Eqs. (5) and (6) the following singly subtractive K-K relations

$$\begin{aligned}&\Re\{\chi^{(n)}(n\omega')\} - \Re\{\chi^{(n)}(n\omega_1)\} \\ &\quad = \frac{2(\omega'^2 - \omega_1^2)}{\pi}\wp\int_0^\infty \frac{\omega\Im\{\chi^{(n)}(n\omega)\}}{(\omega^2 - \omega'^2)(\omega^2 - \omega_1^2)}\mathrm{d}\omega,\end{aligned} \tag{7}$$

$$\begin{aligned}&\omega'^{-1}\Im\{\chi^{(n)}(n\omega')\} - \omega_1^{-1}\Im\{\chi^{(n)}(n\omega_1)\} \\ &\quad = -\frac{2(\omega'^2 - \omega_1^2)}{\pi}\wp\int_0^\infty \frac{\Re\{\chi^{(n)}(n\omega)\}}{(\omega^2 - \omega'^2)(\omega^2 - \omega_1^2)}\mathrm{d}\omega,\end{aligned} \tag{8}$$

which are used for the experimental data analysis

3 Application of singly subtractive K-K relations to experimental data of $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ on polysilane

Here we apply singly subtractive K-K relations for real data, in order to prove their effective relevance. We consider the experimental values of the real and imaginary part of the nonlinear susceptibility of third-order harmonic wave generation on polysilane, obtained by Kishida *et al.* [19]; for both $\Re\{\chi^{(3)}(3\omega;\omega,\omega,\omega)\}$ and $\Im\{\chi^{(3)}(3\omega;\omega,\omega,\omega)\}$, which come from independent measurements, the energy range is $0.4 - 2.5$ eV.

First we consider only data ranging from 0.9 to 1.4 eV, in order to simulate a low-data availability scenario, and compare the quality of the data inversion obtained with the conventional K-K and SSKK relations within this energy range. This interval constitutes a good test since it contains the most relevant feature of both parts of the susceptibility. However, a lot of the spectral structure is left outside the interval and the asymptotic behavior is not established for either parts. Therefore, no plain optimal conditions for optical data inversion are established.

In Fig. 1 we show the results obtained for the real part of the third-order harmonic generation susceptibility. The solid line in Fig. 1 represents the experimental data. The dashed curve in Fig. 1, which was calculated by using conventional K-K relation by truncating integration of (3) consistently gives a poor match with the actual line. On the contrary, we obtain a better agreement with a single anchor point located at $\omega_1 = 0.9$ eV, which is represented by dotted line in Fig. 1. SSKK and measured data for the real part of the susceptibility are almost undistinguishable up to 1.3 eV.

In Fig. 2 similar calculations as above are shown but for the imaginary part of the nonlinear susceptibility. In this case the anchor point is located at $\omega_1 = 1$ eV. From Fig. 2 we observe that the precision of the data inversion is dramatically better by using SSKK instead of the conventional K-K relations. The presence of the anchor point greatly reduces the errors of the estimation performed with the conventional K-K relations in the energy range $0.9 - 1.4$ eV.

4 Conclusions

The extrapolations in K-K analysis, such as the estimation of the data beyond the measured spectral range, can be a serious source of errors [24,25]. Recently, King [26] presented an efficient numerical approach to the evaluation of K-K relations. Nevertheless, the problem of data fitting is always present in regions outside the measured range.

In this paper we proposed how an independent measurement of the unknown part of the complex third-order nonlinear susceptibility for a given frequency relaxes the limitations imposed by the finiteness of the measured spectral range, since in the obtained SSKK relations faster asymptotic decreasing integrands are present. SSKK relations can provide a reliable data inversion procedure based on using *measured data only*. We demonstrated that SSKK relations yield more precise data inversion, using only a single anchor point, than conventional K-K relations.

Naturally it is possible to exploit also MSKK if higher precision is required. However, the measurement of multiple anchor may be experimentally tedious. Finally, we remark that MSKK relations are valid for all holomorphic nonlinear susceptibilities of arbitrary-order. As an example of such holomorphic third-order nonlinear susceptibilities we mention those related to pump and probe nonlinear processes (see details of the various expressions in Ref. [27]). Unfortunately, the degenerate arbitrary-order nonlinear susceptibility is a meromorphic function [28] and MSKK cannot be applied.

Acknowledgments

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Figure captions

Figure 1: Efficacy of SSKK vs. K-K relations in retrieving $\Re\{\chi^{(3)}(3\omega;\omega,\omega,\omega)\}$.

Figure 2: Efficacy of SSKK vs. K-K relations in retrieving $\Im\{\chi^{(3)}(3\omega;\omega,\omega,\omega)\}$.

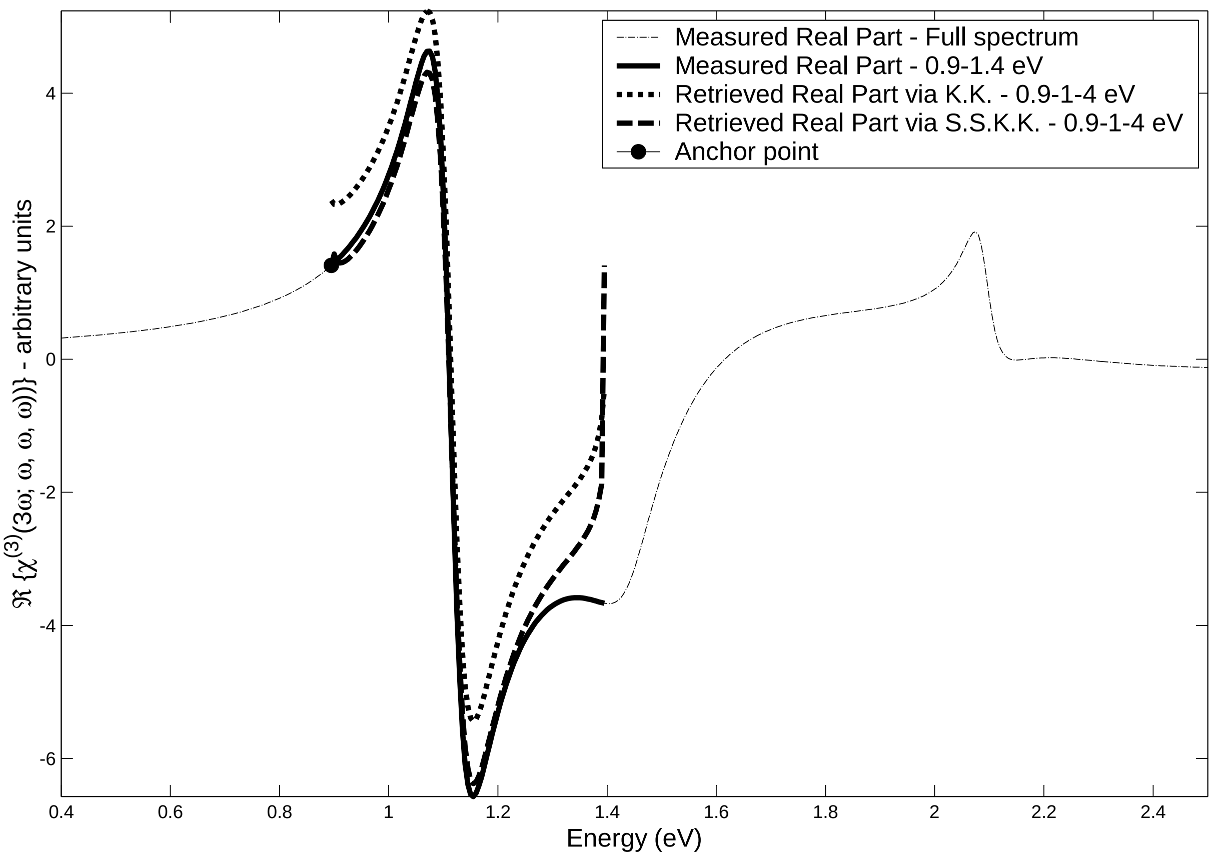

Figure 1: Lucarini, Saarinen, and Peiponen.

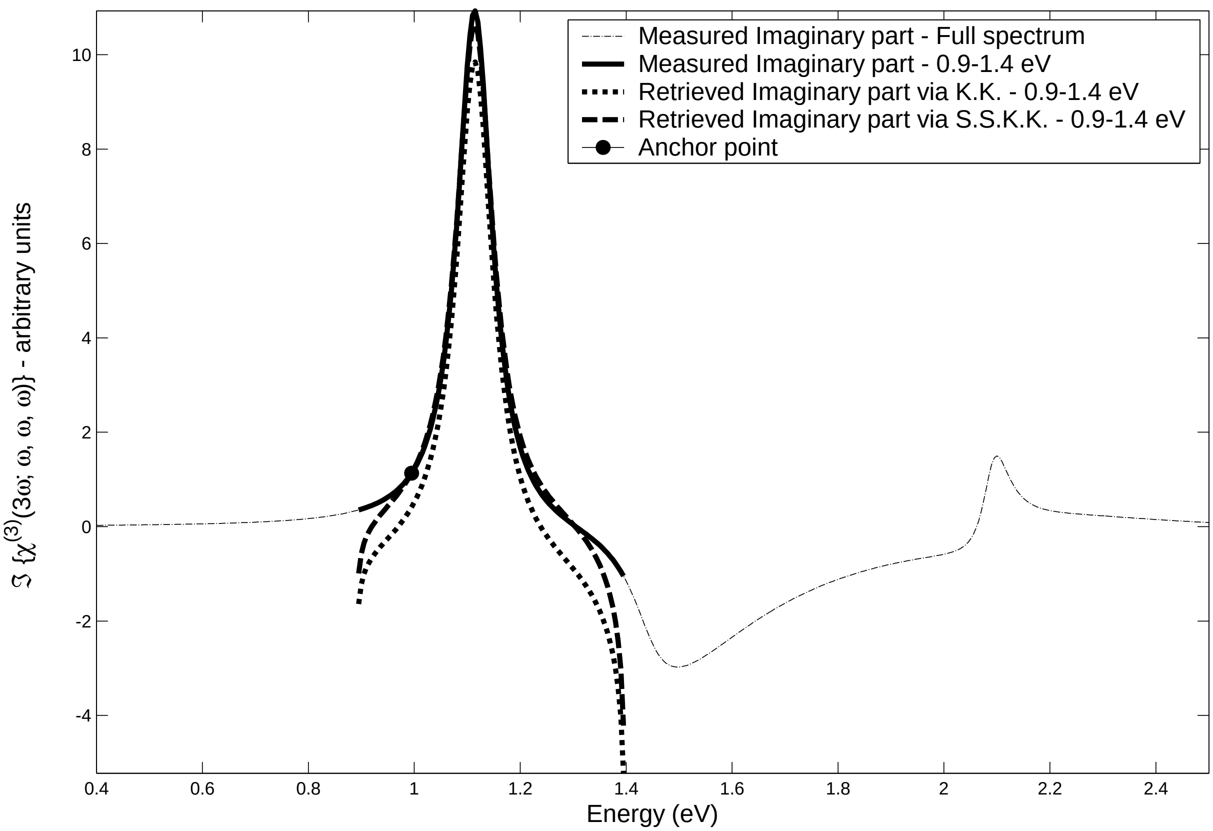

Figure 2: Lucarini, Saarinen, and Peiponen.